TITLE: ADVANCED SOLIDS NMR STUDIES OF OF COAL STRUCTURE AND CHEMISTRY **DATE:** April 1998

PI: Kurt W. Zilm

STUDENT(s): Sean Burns, Anil Mehta, Brett Tounge, Ph.D. Candidates

INSTITUTION: Yale University
Department of Chemistry
350 Edwards Street
New Haven, CT 06511
phone: (203)-432-3956
FAX: (203)-432-6144
email: kurt.zilm@yale.edu

GRANT NO.: DE-FG22-95PC95227

PERIOD OF PERFORMANCE: September 1, 1995 to August 31, 1998

I. ABSTRACT

OBJECTIVE: Advanced solids NMR methods are being developed to improve the quality and accuracy of NMR analysis of coal structure. Applications of these techniques are to be made in a study of the differences between gas-prone and oil-prone coals. Coals known to be sources of waxy crudes from Australia and Indonesia will be compared to North American coals using artificial maturation.

WORK DONE AND CONCLUSIONS: Previous work in our laboratory developed a robust solids NMR spectral editing method for separately acquiring ^{13}C solids NMR spectra of the CH_3, CH_2, CH, and nonprotonated carbon fractions of coals and other organic solids. To achieve better sensitivity in instances where sample sizes are small, i.e. kerogen concentrates, we extended our protocols to higher field NMR operation and developed improved pulse sequences. Using spectral editing data with improved sensitivity provided by our newer techniques, we are able to computer fit the sub-spectral line shapes to a few constituent lines of fixed chemical shift and width. In this manner we are able for instance to quantify the number of phenolic carbon centers in a whole coal. During the last year we have also directed our efforts towards development of the first 800 MHz NMR spectrometer for solid samples. At this record field strength ^{13}C spectra can be acquired in less than 100 scans for model compounds using only 10 milligrams of sample. This greatly increased sensitivity will permit us to utilize solids NMR in a much wider array of chemical investigations of organic source rocks, especially where samples are limited in size.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Solids NMR methods we have developed and are refining provide a detailed quantitative accounting of the functional group distributions present in coals. Development of very high field solids NMR hardware will extend the applicability of our methods to difficult to obtain samples such as single macerals and kerogen concen-

trates. Differences in molecular structure and mobility have been identified between gas-prone and oil prone coals using our editing techniques.

PLANS FOR THE COMING YEAR: During the next year we will concentrate on development of methods for very high field operation. At 800 MHz, magic angle spinning rates of over 24 kHz are required to suppress spinning sidebands in ^{13}C spectra of complex organic source rocks. These high rates complicate dipolar decoupling of the abundant ^{1}H nuclei from the ^{13}C, as well as making cross polarization more difficult. Fortunately we have found solutions to these hurdles, and in fact find that very high spin rates at high fields provides enhanced resolution in many experiments. For instance, in 2 dimensional $^{13}C/^{1}H$ correlation spectra taken at 800 MHz using sample spinning rates of over 20 kHz, we have been able for the very first time to resolve the ^{1}H lines for magnetically inequivalent methylenes in rigid solids. This should prove useful in further investigation of the chemical structure of the mobile methylene component that we find is associated with oil generation by certain coals.

II. HIGHLIGHT ACCOMPLISHMENTS

- A new set of spectral editing methods which work well at higher NMR field strengths have been developed.
- Computer fitting of edited CPMAS subspectra of whole coals demonstrates that a fixed number of bands can be used to describe their complex ^{13}C spectra. This permits the most accurate possible spectroscopic delineation of the various functional groups present in coals.
- A study of the quantitative response of model compound mixtures to spectral editing techniques has found that the editing techniques do not introduce any additional systematic quantitation errors over those present in standard CPMAS NMR.
- A new NMR spectrometer has been developed for high resolution solids work at a record field strength of 18.9 Tesla (800 MHz for ^{1}H).

III. ARTICLES AND PRESENTATIONS

1) Anil Mehta, Brett A. Tounge, and Kurt W. Zilm "Investigation of High Speed CP MAS and Dipolar Recoupling Techniques on Fully Labeled Compounds", presented at the 37th Experimental NMR Conference, Asilomar CA, March 1996.
2) I-Wen Wu, Sean T Burns, Xiaoling Wu, and Kurt W. Zilm "Quantitative Aspects of Solids NMR Spectral Editing", presented at the 37th Experimental NMR Conference, Asilomar CA, Mar. 1996.
3) Sean T. Burns, Xiaoling Wu and Kurt W. Zilm "Improvement of Spectral Editing in Solids: A Sequence for Obtaining CH + CH_2 Only ^{13}C Spectra", presented at the 37th Experimental NMR Conference, Asilomar CA, March 1996.
4) Kurt W. Zilm, Anil Mehta, Brett Tounge, I-Wen Wu, Sean Burns and Xiaoling Wu "CPMAS NMR at High MAS Rates and High Fields" presented at the Eastern Analytical Symposium, Somerset NJ, Nov. 1996.
5) Anil Mehta, Brett Tounge, Sean Burns, Xiaoling Wu, Iwen Wu and Kurt W. Zilm, "High Field CPMAS NMR: Problems And Prospects" presented at the 38th Rocky Mountain Conference, Denver CO, July 1996.
6) Kurt W. Zilm, "High Field CPMAS NMR and Spectral Editing", presented at the Chemagnetics/Otsuka Electronics Solids NMR Workshop, Fort Collins CO, July 1996.
7) Kurt W. Zilm, I-Wen Wu and Xiaoling Wu "Applications of Al-27, P-31 and V-51 MAS Double Resonance Experiments in Catalysis" presented at the FACCS meeting, Providence, RI, November 1997.
8) Kurt W. Zilm "New Approaches to Structure Determination by Solid State NMR: Horizons in Structural Biology" presented at the Department of Chemistry, CalTech, May 13, 1997 and at Department of Chemistry, University of Nebraska, Lincoln NE, November 1997.
9) Kurt W. Zilm "Decoupling, Recoupling and Cross Polarization Spin Dynamics at High MAS Spin Rates" presented at the Eastern Analytical Symposium, Somerset NJ, Nov. 1997.
10) Kurt W. Zilm "Solids NMR of Uniformly Labeled Macromolecular Building Blocks" presented at the Chicago Area NMR Meeting, Argonne National Laboratory, Nov., 1997.
11) Kurt W. Zilm "Problems and Prospects of High Field CPMAS NMR in Structural Biology", presented at the Department of Chemistry, SUNY, Brookhaven, NY, February, 1998.
12) Kurt W. Zilm "Solids NMR of Uniformly Labeled Macromolecular Building Blocks: Challenges at High Fields", presented at the National Science Foundation Workshop on NMR at High Fields, Washington, D.C., February 1998.
13) Kurt W. Zilm "Solids NMR of Uniformly Labeled Macromolecular Building Blocks", presented at the department of Chemistry, University of West Virginia, Morgantown, West Virginia, March, 1998.
14) Kurt W. Zilm "Solids NMR of Uniformly Labeled Macromolecular Building Blocks: Towards Chemical Biology", presented at the 38th Experimental NMR Conference, Asilomar CA, April, 1998.
15) Matthew P. Augustine and Kurt W. Zilm, "Optical Pumping Magnetic Resonance in High Magnetic Fields: Characterization of the Optical Properties of Rb-Xe Mixtures" Mol. Phys. 89, 737-752 (1996).
16) Matthew P. Augustine and Kurt W. Zilm "Observation of Bulk Susceptibility Effects in High Resolution Nuclear Magnetic Resonance" J. Magn. Reson. A, 123, 145-156 (1996).

17) Kenneth B. Wiberg, Jack D. Hammer, Todd A. Keith, and Kurt W. Zilm, "^{13}C NMR Chemical Shifts of Methyl Cation and Anion: A Relationship Between Chemical Shift and Charge" Tetrahedron Letters. 38, 323-326 (1997).
18) Matthew P. Augustine and Kurt W. Zilm "Optical Pumping Magnetic Resonance in High Magnetic Fields: Measurement of High Field Spin Exchange Cross Sections" Chem. Phys. Lett. 280, 24-30, (1997).
19) Sean Burns, Xiaoling Wu and Kurt W. Zilm "Improvements in Spectral Editing CPMAS NMR: The CH + CH_2 Only Experiment", submitted for publication, J. Magn. Reson., (1998).